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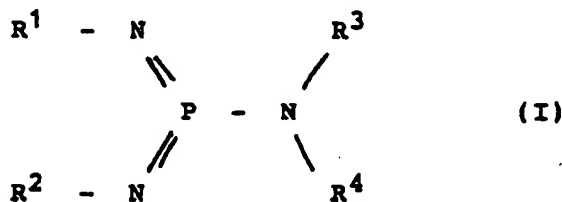
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(54) Polyethylene and method of production thereof.

⑤ A polyethylene, having 1 to 60 methyl branches and 1 to 60 hexyl or higher branches per 1000 carbon atoms, a g-value of 0.5 to 0.8, and a limiting viscosity [η] of 0.005 to 20.0 dl/g as measured at 140° C in o-dichlorobenzene, and a method for producing the same polymerizing ethylene using a catalyst system comprising a coordination nickel compound of zero- or two-valent nickel and an aminobis(imino)phosphorane represented by a general formula (I):



where R¹, R², R³ and R⁴ may be the same or different from each other and represent n-alkyl, isoalkyl, aryl or trialkylsilyl groups, and the polymerization is carried out in the presence of α -olefin.

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POLYETHYLENE AND METHOD OF PRODUCTION THEREOF

Background of the invention:

Field of the invention:

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The present invention relates to a polyethylene having a novel branching structure, and a method of production thereof. More specifically, the present invention relates to production of a polyethylene having a novel branching structure by polymerizing ethylene by employing a special catalyst system with an superior polymerization activity. The polyethylene of the present invention is useful as inflation films, injection-molded articles, blow-molded articles, extrusion-coating materials, polymer blending materials, etc. in the same manner as conventional polyethylenes.

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Description of the Related Art:

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Generally, polymerization of ethylene by a radical initiator at a very high temperature under a very high pressure gives a polyethylene having branched chains of length comparable with that of the main chain thereof. On the other hand, polymerization of ethylene with a Ziegler-Natta catalyst under a low pressure gives a polyethylene having almost no branches.

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For the purpose of producing a branched polyethylene by a method using a Ziegler-Natta catalyst, ethylene is copolymerized generally with an α -olefin. The resulting polyethylene, however, does not have a long branch as that of the polyethylene produced by radical polymerization.

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In an attempt to produce a low-pressure polyethylene having such a long branched chain, ethylene is oligomerized, for example, by a nickel catalyst disclosed in Japanese Laid-Open Patent Application No. 63-12807 (1988), and the resultant oligomers are copolymerized with ethylene by a Cr catalyst. This method, however, does not give a branch having a length comparable with that produced by a radical polymerization.

30 Summary of the invention:

An object of the present invention is to provide a polyethylene having a novel branching structure.

Another object of the present invention is to provide a method for producing a polyethylene having a novel branching structure.

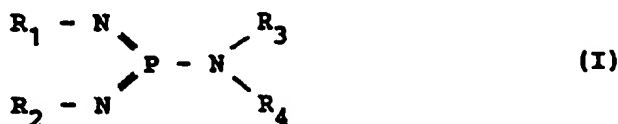
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According to an aspect of the present invention, there is provided a polyethylene, having 1 to 60 methyl branches and 1 to 60 hexyl or higher branches per 1000 carbon atoms, a g-value of 0.5 to 0.8, and a limiting viscosity $[\eta]$ of 0.005 to 20.0 dl/g as measured at 140 °C in o-dichlorobenzene.

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According to another aspect of the present invention, there is provided a method for producing a polyethylene, by polymerizing ethylene employing a catalyst system comprising a coordination nickel compound of zero- or two-valent nickel and an aminobis(imino)phosphorane represented by the general formula (I):

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50 where R_1 , R_2 , R_3 and R_4 may be the same with or different from each other, and are respectively n-alkyl, isoalkyl, aryl or trialkylsilyl, in the presence of an α -olefin.

Brief Description of the Drawings:

Fig. 1 shows the ^{13}C -NMR spectrum of the polyethylene produced in Example 1.

Detailed Description of the Invention:

5 The polyethylene of the present invention as mentioned above is produced by polymerization of ethylene under a low pressure. A polyethylene having such a structure has not been produced under a low pressure until now.

The polyethylene of the present invention has, as short chain branches, 1 to 60 methyl branches and 1 to 60 hexyl or higher branches per 1000 carbons. The existence of such branches is confirmed by ^{13}C -NMR, and the assignment of these branches is made according to, for example, the disclosure of J.C.Randall: J.Polym.Sci., Polym.Phys.Ed., 11, 275 (1973).

The existence of long chain branches in the structure of the polyethylene is suggested, if the polyethylene has a g-value of less than 1: the g-value being defined by $g = [\eta]/[\eta]_l$, where $[\eta]_l$ denotes a limiting viscosity of a linear polyethylene and $[\eta]$ denotes a limiting viscosity of the branched polyethylene having the same melt index. The polyethylene of the present invention has a g-value of from 0.5 to 0.8, which suggests the existence of long chain branches having a chain length comparable with the length of the main chain. The polyethylene of the present invention has substantially no ethyl branch and butyl branch which are found in the polyethylenes produced by radical polymerization at a high temperature under a high pressure, or the number of the branches having 2 to 5 carbon atoms in the polyethylene of the present invention is not more than 1 per 1000 carbon atoms, which also evidences the definite novelty of the present invention.

The method for producing the polyethylene is described below.

In the present invention, specific examples of the coordination nickel compounds of zero- or two-valent nickel include biscyclooctadienenickel, cyclododecatrienenickel, cyclooctatetraenenickel, bisallylnickel, etc.

25 The aminobis(imino)phosphoranes represented by the general formula (I) specifically includes bis-(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane, etc. These compounds can be prepared by the method, for example, described by O.J.Scherer, N.Kush: Chem. Ber. 107, 2123 (1974).

In polymerization of ethylene employing the two component catalyst system, the ratio of the nickel compound and the aminobis(imino)phosphorane is preferably in the range of from 1:1 to 1:100 (in molar ratio). The respective components may be introduced into the polymerization vessel either in a form of an undissolved solid or in a form of a solution in a solvent, and the order of addition does not affect the structure of the polymer and the activity of the catalyst.

30 The α -olefin to be added in the polymerization of ethylene is preferably an α -olefin having from 3 to 20 carbons. The specific examples are propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, etc. The amount of the α -olefin to be used is not limited. However, the use thereof in an amount equimolar to nickel or more gives improvement of the catalyst activity. The α -olefin may be used also as a solvent for polymerization.

40 The polymerization of ethylene may be practiced either in a liquid phase or in a gas phase. The polymerization in a liquid phase is preferably conducted in an inert solvent. The inert solvent may be any of the solvents which are used in the related technical field, such as aliphatic hydrocarbons of 4 to 20 carbons, aromatic hydrocarbons, halogenated hydrocarbons. The specific examples are hexane, heptane, pentane, octane, decane, cyclohexane, benzene, toluene, xylene, chlorobenzene, ethylene dichloride, kerosene, etc.

The preferable polymerization conditions in the present invention are a polymerization temperature of from -78 to 200°C , and a polymerization pressure of from 1 to $200\text{ kg/cm}^2\text{G}$.

Detailed Description of the Preferred Embodiments:

50 The present invention is described below in more detail referring to examples without limiting it in any way.

Regarding the structure of the polyethylene produced according to the present invention, the short chain branches are identified by ^{13}C -NMR with the assignment on the basis of J.C.Randall: J.Polym.Sci., Polym.Phys. Ed., 11, 275 (1973).

55 The existence of long chain branches in the structure of the polyethylene is indicated by the value of $g = [\eta]/[\eta]_l$, where $[\eta]_l$ denotes a limiting viscosity of a linear polyethylene and $[\eta]$ denotes a limiting viscosity of the branched polyethylene having the same melt index. The g-value of less than 1 suggests the existence of long chain branches.

Example 1

Into a 2-liter magnetic-stirrer-type stainless steel reactor, which had been purged sufficiently with nitrogen, there were added 500 ml of toluene, 2.0 mmol of bis(1,5-cyclooctadiene)nickel, and 2.0 mmol of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane. The inside temperature was adjusted to 20 °C. Thereto 85 ml of 1-hexene was added. Then ethylene was fed to maintain the inside pressure at 25 kg/cm²G, and to cause polymerization reaction for 3 hours.

After completion of the reaction, the unreacted ethylene was removed, and the catalyst was decomposed with a hydrochloric acid solution in methanol. The reaction mixture was poured into methanol to recover the polymer. The recovered polymer was dried under vacuum for 8 hours to give 130 g of polymer. The melting point was 94.5 °C as determined by differential scanning calorimeter (DSC), and the limiting viscosity was 1.08 dl/g at 140 °C in dichlorobenzene.

Fig. 1 shows the ¹³C-NMR spectrum of the resulting polymer. The peaks resulting from methyl branches are found at 20.4 ppm, 27.5 ppm, 30.4 ppm, 33.2 ppm, and 37.5 ppm, and those resulting from hexyl and higher branches are found at 14.3 ppm, 23.1 ppm, 27.4 ppm, 30.7 ppm, 32.4 ppm, 34.6 ppm, and 38.3 ppm. No other peak resulting from a branched structure is observed. From the spectrum, the number of the methyl branches and the hexyl and higher branches are found to be respectively 22 per 1000 carbon atoms. No branches having 2 to 5 carbons was found in the polymer. The g-value was 0.70.

Example 2

Into a 2-liter magnetic-stirrer-type stainless steel reactor, which had been purged sufficiently with nitrogen, there were added 500 ml of toluene, 2.0 mmol of bis(1,5-cyclooctadiene)nickel, and 2.0 mmol of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane. The inside temperature was adjusted to 20 °C. Thereto 50 ml of 1-butene was added. Then ethylene was fed to maintain the inside pressure at 25 kg/cm²G, and to cause polymerization reaction for 3 hours.

After completion of the reaction, the unreacted ethylene was removed, and the catalyst was decomposed with a hydrochloric acid solution in methanol. The reaction mixture was poured into methanol to recover the polymer. The recovered polymer was dried under vacuum for 8 hours to give 140 g of polymer. The melting point was 93.8 °C as determined by DSC, and the limiting viscosity was 0.86 dl/g at 140 °C in dichlorobenzene.

The number of the methyl branches was found to be 23 per 1000 carbons and the number of the hexyl and higher branches were found to be 24 per 1000 carbon atoms. No branches having 2 to 5 carbons was found in the polymer. The g-value was 0.69.

Example 3

Into a 2-liter magnetic-stirrer-type stainless steel reactor, which had been purged sufficiently with nitrogen, there were added 500 ml of toluene, 1.3 mmol of bis(1,5-cyclooctadiene)nickel, and 1.3 mmol of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane. The inside temperature was adjusted to 20 °C. Thereto 47 ml of 1-decene was added. Then ethylene was fed to maintain the inside pressure at 25 kg/cm²G, and to cause polymerization reaction for 24 hours.

After completion of the reaction, the unreacted ethylene was removed, and the catalyst was decomposed with a hydrochloric acid solution in methanol. The reaction mixture was poured into methanol to recover the polymer. The recovered polymer was dried under vacuum for 8 hours to give 60 g of polymer. The melting point was 92.5 °C as determined by DSC, and the limiting viscosity was 1.03 dl/g at 140 °C in dichlorobenzene.

The number of the methyl branches was found to be 18 per 1000 carbons and the number of the hexyl and higher branches were found to be 18 per 1000 carbon atoms. No branches having 2 to 5 carbons was found in the polymer. The g-value was 0.73.

Example 4

Into a 2-liter magnetic-stirrer-type stainless steel reactor, which had been purged sufficiently with nitrogen, there were added 500 ml of toluene, 2.0 mmol of bis(1,5-cyclooctadiene)nickel, and 2.0 mmol of

bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane. The inside temperature was adjusted to 20 °C. There to 65 ml of 4-methyl-1-pentene was added. Then ethylene was fed to maintain the inside pressure at 25 kg/cm²G, and to cause polymerization reaction for 3 hours.

After completion of the reaction, the unreacted ethylene was removed, and the catalyst was decomposed with a hydrochloric acid solution in methanol. The reaction mixture was poured into methanol to recover the polymer. The recovered polymer was dried under vacuum for 8 hours to give 120 g of polymer. The melting point was 94.1 °C as determined by DSC, and the limiting viscosity was 1.15 dl/g at 140 °C in dichlorobenzene.

The number of the methyl branches was found to be 21 per 1000 carbons and the number of the hexyl and higher branches were found to be 22 per 1000 carbon atoms. No branches having 2 to 5 carbons was found in the polymer. The g-value was 0.88.

Example 5

Into a 2-liter magnetic-stirrer-type stainless steel reactor, which had been purged sufficiently with nitrogen, there were added 500 ml of toluene, 2.0 mmol of bis(1,5-cyclooctadiene)nickel, and 2.0 mmol of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane. The inside temperature was adjusted to 20 °C. There to 5 ml of 1-butene was added. Then ethylene was fed to maintain the inside pressure at 25 kg/cm²G, and to cause polymerization reaction for 3 hours.

After completion of the reaction, the unreacted ethylene was removed, and the catalyst was decomposed with a hydrochloric acid solution in methanol. The reaction mixture was poured into methanol to recover the polymer. The recovered polymer was dried under vacuum for 8 hours to give 105 g of polymer. The melting point was 90.3 °C as determined by DSC, and the limiting viscosity was 1.12 dl/g at 140 °C in dichlorobenzene.

The number of the methyl branches and the number of the hexyl and higher branches were found respectively to be 20 per 1000 carbons. No branches having 2 to 5 carbons was found in the polymer. The g-value was 0.87.

Example 6:

Ethylene was polymerized in the same manner as in Example 1 except that 1-hexene used in Example 1 was not added. 16 g of polymer was produced.

The polymer thus produced showed a melting point of 88.3°C, and a limiting viscosity of 1.93dl/g. The number of the methyl branches and the number of the hexyl and higher branches were found respectively to be 20 per 1000 carbons, and no branches having 2 to 5 carbons were found in the polymer. The g-value was 0.70.

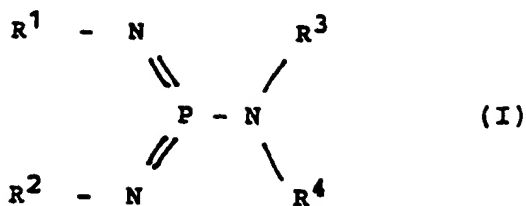
Claims

1. A polyethylene, characterised in that it has 1 to 60 methyl branches and 1 to 60 hexyl or higher branches per 1000 carbon atoms, a g-value of less than 1 and a limiting viscosity [η] of 0.005 to 20.0 dl/g as measured at 140 °C in o-dichlorobenzene.

2. A polyethylene as claimed in Claim 1 characterised in having a g-value of 0.5 to 0.8.

3. A polyethylene as claimed in Claim 1 or Claim 2 characterised in that it has substantially no C₂-C₅ branches as determined by ¹³C-NMR spectroscopy.

4. A method for producing a polyethylene by polymerizing ethylene characterised in that it uses a catalyst system comprising a coordination nickel compound of zero- or two-valent nickel and an aminobis-(imino)phosphorane represented by a general formula (I):



where R^1 , R^2 , R^3 and R^4 may be the same or different from each other and represent n-alkyl, isoalkyl, aryl or trialkylsilyl groups and the polymerisation is carried out in the presence of α -olefin.

5. A method as claimed in Claim 4 characterised in that the coordination nickel compound is selected from the group consisting of bis(cyclooctadiene)nickel, cyclododecatriene nickel, cyclooctatetraene nickel and bisallylnickel.

6. A method as claimed in Claim 4 or Claim 5 characterised in that the aminobis(imino)phosphorane is bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane.

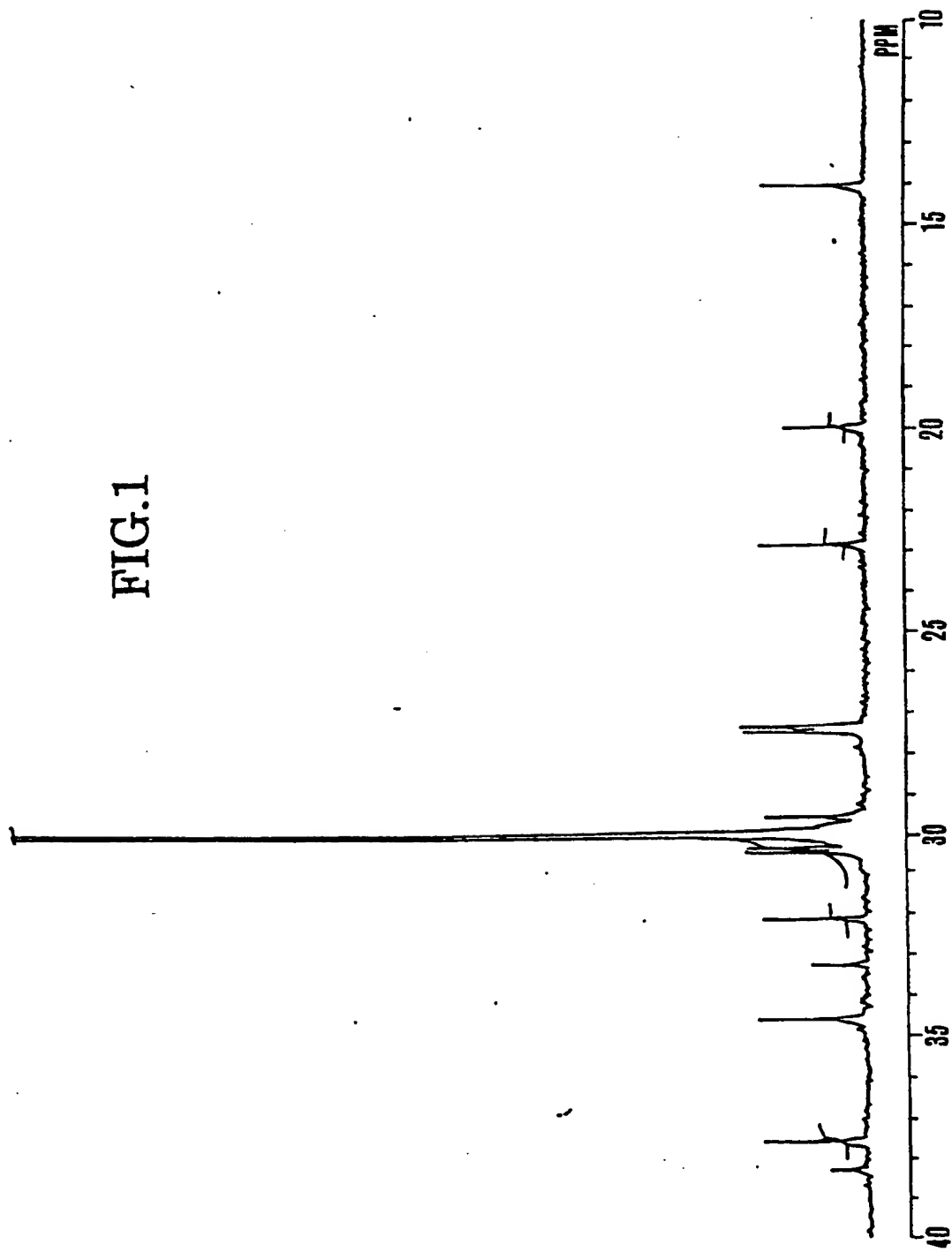
7. A method as claimed in Claim 4, 5 or 6 characterised in that the molar ratio of the coordination nickel compound to the aminobis(imino)phosphorane is 1:1 to 1:100.

8. A method as claimed in Claim 4, 5, 6 or 7 characterised in that the α -olefin has 3 to 20 carbons.

9. A method as claimed in any one of Claims 4 to 8 characterised in that the polymerisation is done at a temperature ranging from -78 to 200°C .

10. A method as claimed in any one of Claims 4 to 9 characterised in that the polymerization is done at a pressure ranging from 1 to 200 kg/cm²G.

FIG.1



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